Science of the Total Environment 568 (2016) 566–577

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Temporal variability of micro-organic contaminants in lowland chalk catchments: New insights into contaminant sources and hydrological processes

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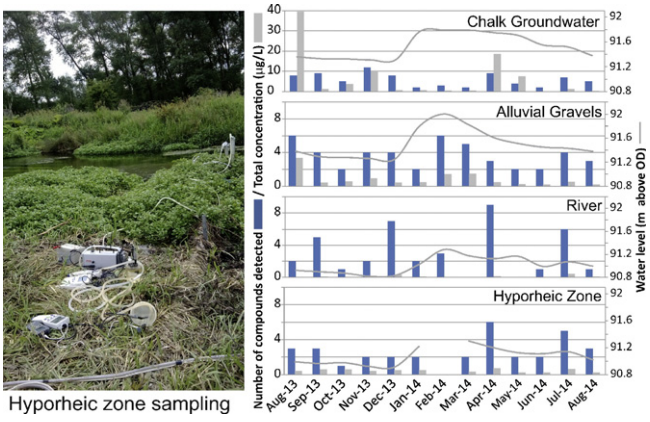
HIGHLIGHTS

- Trace microorganics found in all hydrological compartments in a chalk lowland catchment
- Greatest number of compounds found in Chalk groundwater compared to surface water
- The hyporheic zone shown to be important for MO contaminant attenuation
- High temporal variability has implications for the design of monitoring programmes.

GRAPHICAL ABSTRACT



Hyporheic zone sampling

ARTICLE INFO

Article history:
Received 7 December 2015
Received in revised form 22 January 2016
Accepted 22 January 2016
Available online 2 February 2016

Keywords:
Micro-organics
Emerging contaminant
High flow
Hydrogeological compartments
Chalk

ABSTRACT

This paper explores the temporal variation of a broad suite of micro organic (MO) compounds within hydrologically linked compartments of a lowland Chalk catchment, the most important drinking water aquifer in the UK. It presents an assessment of results from relatively high frequency monitoring at a well-characterised site, including the type and concentrations of compounds detected and how they change under different hydrological conditions including exceptionally high groundwater levels and river flow conditions during 2014 and subsequent recovery. This study shows for the first time that within the Chalk groundwater there can be a greater diversity of the MOs compared to surface waters. Within the Chalk 26 different compounds were detected over the duration of the study compared to 17 in the surface water. Plasticisers (0.06–39 µg/L) were found to dominate in the Chalk groundwater on 5 visits (38.4%) accounting for 14.5% of detections but contributing highest concentrations whilst other compounds dominated in the surface water. Trichloroethene and atrazine were among the most frequently detected compounds. The limit for the total pesticide concentration detected did not exceed EU/UK prescribed concentration values for drinking water. Emerging organic compounds such as caffeine, which currently do not have water quality limits, were also detected. The low numbers of compounds found within the hyporheic zone highlight the role of this transient interface in the attenuation and breakdown of the MOs, and provision of an important ecosystem service.

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http://dx.doi.org/10.1016/j.scitotenv.2016.01.146

1. Introduction

In the last few decades there has been a growing interest in the occurrence of micro-organic (MO) contaminants in the terrestrial and aquatic environment, and in their environmental fate and potential toxicity (Halling-Sørensen et al., 1998; Kolpin et al., 2002; Kümmerer, 2009). The contamination of groundwater by MOs is a growing concern and relatively poorly understood compared to other freshwater resources. It is clear from recent studies that trace concentrations of a large range of compounds can be detected in groundwater (Focazio et al., 2008; Lapworth et al., 2012; Loos et al., 2010; Stuart et al., 2012). This continues to be a global problem (Brausch and Rand, 2011; Jurado et al., 2012; Luo et al., 2014). A limited but growing number of studies are using MOs as tracers to fingerprint contaminant sources in surface water and groundwater and understand the transient nature of MOs processing at the groundwater–surface water interface (GSI) (e.g.Buerge et al., 2003; Burke et al., 2011; Engelhardt et al., 2011; Sorensen et al., 2014; Stuart et al., 2014).

A number of recent studies looking at MOs in vulnerable Chalk karstic systems have been published (Hillebrand et al., 2014; Reh et al., 2013), as well as studies focussed on the attenuation of selected MOs by Hillebrand et al. (2015). Research in these karstic settings has highlighted the transient nature of MO contamination and shows the need for greater temporal resolution if effective monitoring is to be undertaken in comparable hydrologic settings. A recent regional analysis of MO occurrence has been carried out for the Chalk of England and France (Lapworth et al., 2015), but this did not have a temporal component and to date there have been very few studies focussed on characterising the temporal variation of both the types and concentrations of MOs, including emerging organic contaminants, present in groundwater and the GSI in lowland chalk settings. In addition, with the development of broad screening techniques (e.g. Lapworth et al., 2015; Wode et al., 2015) it is no longer necessary to be restricted to small numbers of target compounds as has often been the case in previous studies to date.

The Chalk is the most important aquifer system in the UK, and in parts of England is the dominant source of drinking water (Defra, 2015). In the south east of England it can provide up to 80% of the drinking water supply, this area being classified as one of the regions globally with the lowest water availability due to high population density and relatively low rainfall (RGS, 2012). More widely, the Chalk aquifers of north-west Europe form a hugely important natural resource, providing drinking water and sustaining river flows across a large part of southern England and northern France as well as parts of Belgium, Germany, the Netherlands and Denmark. Discharge from the Chalk aquifer sustains river flow and groundwater dependent wetlands and groundwater dependent terrestrial ecosystem which require assessment under the Water Framework Directive (Directive 2000/60/EC). As such it is important to understand the nature, types and concentrations of the MOs found within Chalk groundwater (Lapworth et al., 2015), and in particular at the groundwater/surface water interface, to understand how these change over the hydrological year as well as in response to under the high flow conditions of early 2014. Recent research undertaken at bank infiltration sites in the UK (Ascott et al., 2015) has shown that following extreme high flow conditions it can take up to six months for water quality to return back to baseline conditions.

Both point and diffuse sources of MOs, including emerging compounds, contribute to contamination of groundwater. Factors controlling their entry to groundwater include land use and climate as well as the management of liquid and solid waste and treatment by-products (Bloomfield et al., 2006; Kümmerer, 2009; Schwarzbauer et al., 2002). The fate and concentrations of MOs in groundwater depend on a number of physicochemical processes, including sorption and degradation, as well as the hydrogeological setting including amount and distribution of groundwater recharge, residence times and pathways (Lapworth et al., 2012). The fate of MOs in the hyporheic zone (HZ, the zone of interaction between surface water and groundwater) is an important area of ongoing research (e.g. Lewandowski et al., 2011; Lu et al., 2015a, 2015b; Ward et al., 2015), this is due to its transient flow dynamics; relatively high microbiological activity and reduced phototransformation potential (compared to surface waters). This zone has a capacity to attenuate organic pollution within the river-groundwater continuum (Freitas et al., 2015), and providing an important ecosystem service (Griebler and Avramov, 2015).

This study was carried out at a well-characterised lowland Chalk research observatory in Southern England (Allen et al., 2010). The aims of this study were to determine i) how MO number and concentrations vary through the hydrogeological year ii) in particular whether there is a relationship between any variation observed and groundwater level fluctuations including during hydrological extreme conditions iii) the seasonal variability of the role of the hyporheic zone (HZ) in MO attenuation.

2. Study site

The study was conducted at the Boxford research site in Berkshire, UK. The site was instrumented with piezometers as part of the Lowland Catchment Research Programme (LOCAR) (Wheater and Peach, 2004), in order to characterise the interaction between groundwater, surface water and hyporheic zone in a lowland Chalk catchment (Allen et al., 2010). The site is rural, to the north of it lies a farm which undertakes both arable and dairy activities, while to the south lies the River Lambourn and an associated wetland, both designated as a Site of Special Scientific Interest (SSSI).

2.1. Hydrogeological setting

The geology of the underlying strata is shown in Fig. 1a and comprises Cretaceous Newhaven Chalk Formation overlain by superficial deposits of variable fractions of gravel and sand. The Newhaven Chalk is a soft microporous limestone with fracture and matrix flow both playing a role in movement of groundwater, which can be complex. The superficial deposits are of heterogeneous nature, alluvium with sand and gravel layers with discontinuous peat lenses present beneath the site. Head deposits, a term used to describe a diamicton of poorly-sorted chalk gravel, sand and silt, which are deposited due to periglacial mass flow movement, are found along the sides of and base of valleys in the chalk downs of southern England, see Newell et al. (2015) and references therein for further details on the geology of this area.

Interactions between the surface water and groundwater have been established by Allen et al. (2010), with hydraulic connectivity between the River Lambourn and the superficial gravels as well as the Chalk, these are schematically represented in Fig. 1b including the regional groundwater flow and stage dependant lateral and hyporheic exchange. There is however poor connectivity in the vicinity of the riverbank between the gravels and the Chalk. This is a result of lower permeability due to reworked chalk at the chalk–gravel interface. The overall groundwater flow direction is to the south and within the site is towards the river. A chalk mound present in the vicinity of the Y piezometer (Fig. 1b).

The established behaviour of these interactions during high and low water level is summarised below. During low water level conditions, there is notable input to the river from the Chalk as well as the gravels and alluvium from both southerly and northerly directions. During high water levels the proportion to the River from the Chalk is smaller and there is movement from the river to the gravels and alluvium to the south. The southerly flow of groundwater within the Chalk under the riverbed provides significant groundwater contributions within the wetland adjacent to the River Lambourn (Chambers et al., 2014).

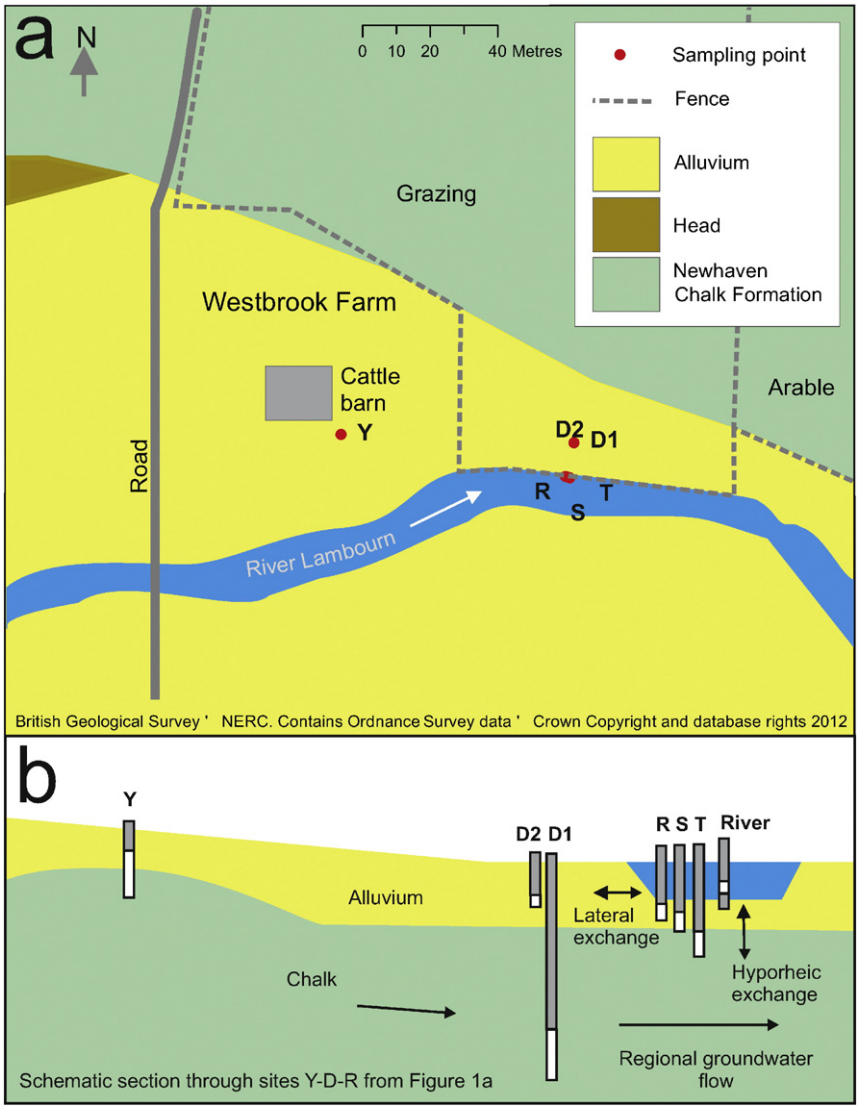

Fig. 1. a) Map of site area showing geological setting, sample locations and cross section for low groundwater level conditions, b) schematic cross section Y–D–R and groundwater flow regime.

2.2. Groundwater sampling

Groundwater sampling was carried out of 6 piezometers (see Fig. 1) and the River Lambourn, a summary of the piezometer completion details are shown in Table 1. The 6 piezometers included one completed within the Chalk (D1) which was 25.1 m deep, and two within gravels (D2 and Y) 3.6 and 3.5 m deep respectively. The three within the HZ, R, S and T, are completed at different depths below the river bed surface, 0.5 m, 1.5 m and 2.5 m respectively (Allen et al., 2010). The piezometers together sample groundwater from 0.5 m to 25 m depth and offer insight into different hydrological compartments within the site which may be influenced by different pollution sources and pathways. The HZ piezometers have a steel casing while the others have plastic casing.

3. Method

3.1. Sampling

Water sampling was carried out between August 2013 and August 2014 by means of 13 regular monthly site visits. This captured the full hydrological cycle, including a period of extremely high groundwater levels during February 2014 and subsequent recovery. This provided a novel opportunity to acquire a dataset which is both frequent and covers a range of hydrologic conditions.

Piezometers were purged with a submersible pump to ensure a fresh groundwater sample was obtained, and unstable field parameters — pH, electrical conductivity, dissolved oxygen and redox potential were monitored until they had stabilised. Samples were then collected using dedicated PTFE tubing and a peristaltic pump. The tubing was cleaned using a surfactant prior to sampling and rinsed with ultrapure water. Samples were pumped through the dedicated tubing for

Table 1
Details of groundwater sampling sites used in this study.

Name	Easting	Northing	Depth (m)	Top of casing (m aOD)	Bottom of casing (m aOD)	Geology of response zone
D1	442802	172297	25.13	92.01	91.18	Chalk
D2	442802	172297	3.64	92.01	91.17	Gravel
R	442800	172286	3.09	91.78	91.58	Hyporheic
S	442801	172285	3.29	91.84	91.64	Hyporheic
T	442802	172285	4.33	91.94	91.74	Hyporheic
Y	442733	172298	3.55	92.53	91.68	Gravel

over 10 min before collecting the sample. Samples were collected in pre-cleaned 1-litre glass bottles with PTFE-lined caps provided by the UK Environment Agency National Laboratory Service (NLS). These steps were undertaken to prevent contamination from tubing to ensure sample collected was representative of the setting. The sampling order of the piezometers was varied to ensure any "memory effect" was counteracted. The same tubing and peristaltic pump were used to collect surface water samples to ensure consistency. PTFE tubing was used as it leaches less plasticiser compounds compared to other more flexible tubing.

Staff undertaking sampling in the field followed strict protocol to ensure no personal care products were introduced. Gloves were not used during sampling to reduce potential contamination from plasticisers. Samples were stored in a refrigerator and sent for analysis as quickly as was practicable in order to minimise storage time and therefore potential for breakdown of compounds. For more details on the method see Stuart et al. (2014).

Water level data were collected from each piezometer at the beginning of each site visit and monthly stage readings were used to estimate water levels within the River Lambourn. The water level for the Chalk (D1) piezometer between January and March was estimated by measuring against external casing flange as it was artesian. Due to exceptionally high rainfall and river water levels/flow experienced during February 2013, sampling of the HZ piezometers was not possible.

3.2. Chemical analysis and QC

Analysis was conducted by the Environment Agency NLS using a multi-residue GC–MS method which screens for over 1000 organic compounds. An internal standard phenanthrene-d10 was added to each sample at the start of analysis to correct for any loss of compound during the sample preparation or inlet stage. Due to the wide range of compounds contained within the target database and their variety of chemical characteristics, a double liquid–liquid extraction method was used, (neutral-acid) with dichloromethane. The combined extracts were then concentrated to 1 mL using a Zymark Turbo-Vap®, dried and transferred to an auto-sampler vial for analysis.

The detection limits were within 0.01–0.1 μg/L for 90% of compounds, with a reporting limit of 0.01 μg/L for 75% of compounds. To improve the accuracy of concentration reported, a response was obtained from running a reference standard for each individual target compound at a known concentration, typically 1 μg/L, this provides a fixed single point calibration. NLS participate in the UKAS accredited proficiency scheme Aquacheck, specifically Group 22, the qualitative organics by GC–MS.

A field blank sample was collected for each of the monthly visits using the same equipment as that used in the field and ultra-pure water to establish what, if any, MOs were introduced by the method itself. The blanks were sent for analysis with the 7 monthly samples which included two gravel samples Y and D2, chalk D1, surface water from the river – sample SW and three hyporheic zone samples – R, S and T.

Reported data received from NLS had been corrected for any contamination from within the Laboratory itself. These data were further examined against the field blanks. The compounds that were found in the blank are highlighted in the Supplementary material in Table S1. Plasticisers were most common among the 49 detects of the 15 compounds found within the blanks during 13 visits. N-butyl-4-methyl benzenesulfonamide (BBSA) and dimethyl phthalate (DMP) were the most frequently detected compounds both detected on 11 visits. The two compounds with highest concentrations were BBSA with a maximum concentration of 1400 μg/L and bis(2-ethylhexyl) phthalate (DEHP) with 8 μg/L. The number of compounds detected within the blank varied between 1 and 7. The decision was made to exclude all the compounds found within the blanks as there can be no certainty as to their provenance, as a result they are not considered further in this paper. The information on their detection frequency, maximum, minimum and median concentrations are included in Supplementary material for completeness (Table S1).

The analytical technique used does not separate or detect a range of polar MOs. These could include important compounds such as the beta blockers, penicillin related antibiotics, fenofibrate, hydrocortisone, salbutamol and other pharmaceuticals as well as perfluoro surfactants and a number of pesticides and hormones. Many biologically active compounds are chiral, and may have two enantiomers, or even two pairs. They may be synthesised as racemic mixtures, although individual enantiomers may differ widely in environmental impact and toxicity (Petrie et al., 2014). Chiral examples reported in other studies to be found in surface water include mecoprop, ibuprofen and ephedrine. Screening techniques, such as used in the present study are not able to distinguish between enantiomers.

4. Results

4.1. MO detection frequency

4.1.1. Numbers of MOs detected

Having excluded the data for compounds found within the blanks, 303 detections of 39 different chemical compounds in the 87 samples collected from 6 piezometers and the river. Of these 39 MOs, 19 compounds were detected more than once. A summary of the compounds detected (blank excluded), their use, number of times compounds and the percentage of time detected, their maximum and minimum concentrations and their octanol/water partition coefficient (K_{ow}) are presented in Table 2.

MO occurrence is dominated by established pollutants, the chlorinated solvent trichloroethene (TCE), the herbicides atrazine and simazine, and the transformation product atrazine desethyl accounted for four of the top six. Bisphenol A (BPA), a plasticiser and known endocrine disruptor and two polyaromatic hydrocarbons, fluoranthene and pyrene, were also frequently detected. The emerging contaminants caffeine and butylated hydroxytoluene (BHT) (a food additive) were also in the top ten.

Plasticisers are greyed out in Table 2; plasticisers are widely detected compounds and it is difficult to categorically attribute their source. The plastic materials used in the construction of the piezometers may be contributing to the plasticisers detected.

4.1.2. Number of compounds detected in different hydrological compartments

The highest number of MOs detected was in the Chalk where 26 different compounds were found with a maximum of 12 different compounds in one sample. Surface water samples had 17 compounds detected overall, the second highest number with a maximum of 9 compounds detected on one occasion. For alluvial groundwater, within the gravel piezometer Y overall 11 compounds were detected with a maximum of 6 detected per visit while in D2 10 compounds were detected overall and 7 was the maximum number of compounds detected per sample. Fewer compounds were detected within the HZ samples; in R overall 6 different compounds with a maximum of 4 per visit, in S 8 compounds were detected overall with a maximum of 5 per visit and in T overall 9 compounds and maximum of 6 detected on a single visit.

4.1.3. Temporal variations in detection frequency

Overall there were clear temporal variations, with the lowest number of compounds detected during the period of highest water levels within the chalk D1 piezometer. From August 2013 to December 2013, when water levels were low, between 5 and 12 compounds were detected (median 8) on each visit, which was significantly higher than during the high water level period in January to May 2014 when between 2 and 9 compounds were detected (median 3). Within the gravel piezometers (D2 and Y) there was a similar pattern with lower

Table 2
Summary of detection frequency, concentrations, and properties for compounds detected during the study ordered by frequency of detection.

Chemical compound name	CAS number	Use	Detections		Concentration (μg/L)			Log K_{ow}
			No.	%	Max	Min	Median	
Trichloroethene (TCE)	79-01-6	Solvent/medical	76	25.08	0.90	0.03	0.35	2.29
Atrazine	1912-24-9	Herbicide	68	22.44	0.05	0.01	0.02	2.75
Atrazine desethyl	6190-65-4	Breakdown product of a trazine	24	7.92	0.05	0.01	0.03	1.51
Bisphenol A (BPA)	80-05-7	Plastic production	17	5.61	39.00	0.02	0.20	3.32
2-Chlorophenyl isocyanate	3320-83-0	Pesticide intermediate/agrochemical/ pharmaceutical	17	5.61	0.85	0.10	0.40	3.24
Simazine	122-34-9	Herbicide	16	5.28	0.02	0.01	0.01	2.41
Fluoranthene	206-44-0	Combustion product	12	3.96	0.03	0.01	0.01	5.16
Pyrene	129-00-0	Combustion/dyes manufacturing	12	3.96	0.02	0.01	0.01	5.11
Caffeine	58-08-2	Stimulant/food	7	2.31	0.10	0.02	0.04	0.07
Butylated hydroxytoluene (BHT)	128-37-0	Food additive	6	1.98	0.20	0.04	0.10	5.10
Terpinyl acetate	80-26-2	Cosmetics/fragrance	5	1.65	0.01	0.01	0.01	3.96
Diisobutyl phthalate (DIBP)	84-69-5	Plasticiser	4	1.32	5.00	0.70	1.20	0.80
Chrysene	218-01-9	Dye manufacturing/coal tar/wood preservative	4	1.32	0.01	0.01	0.01	5.86
Benz[a]anthracene	56-55-3	Coal tar, food additive, exhaust fumes	4	1.32	0.01	0.01	0.01	5.70
1(3H)-isobenzofuranone	87412	Cosmetics	3	0.99	0.03	0.01	0.02	4.31
Drometrizole	2440-22-4	Cosmetics/sun screen	2	0.66	0.15	0.08	0.12	4.30
Diphenyl sulphide	139-66-2	Pesticide	2	0.66	0.13	0.07	0.10	4.45
N,N,N',N'-Tetraacetylethylenediamine(TAED)	110-18-9	Catalyst	2	0.66	0.03	0.03	0.03	-2.36
1,3,5-Trially-1,3,5-triazine-2,4,6 trione (TTT)	1025-15-6	Antiprotozoal-veterinary use	2	0.66	0.01	0.01	0.01	5.12
Caprolactam	105-60-2	Nylon precursor, synthetic polymer/plastics	1	0.33	3.00	3.00	3.00	0.66
Di-n-butyl phthalate(DNBP)	84-74-2	Plasticiser	1	0.33	1.00	1.00	1.00	3.70–4.72
Diethyl phthalate (DEP)	84-66-2	Solvent/plasticiser/cosmetics	1	0.33	1.00	1.00	1.00	2.50
Propyzamide	23950-58-5	Herbicide	1	0.33	0.20	0.20	0.20	3.1–3.2
Butylated hydroxyanisole (BHA)	25013-16-5;	Antioxidant, food additive, cosmetics,	1	0.33	0.07	0.07	0.07	5.10
	88-43-4	petroleum						
Tri-(2-chloroethyl) phosphate	115-96-8	Plasticiser/flame retardant	1	0.33	0.06	0.06	0.06	1.78
Phthalic anhydride	85-44-9	Plasticiser	1	0.33	0.06	0.06	0.06	1.60
Tributyl phosphate(TBP)	126-73-8	Plasticiser	1	0.33	0.05	0.05	0.05	4.00
Triphenyl phosphate	115-86-6	Plasticiser/fire retardant	1	0.33	0.05	0.05	0.05	4.61–4.76
Benzothiazole	95-16-9	Drugs, dyes	1	0.33	0.04	0.04	0.04	2.01
Carbamazepine	298-46-4	Pharmaceutical (epilepsy and mood drug)	1	0.33	0.04	0.04	0.04	3.79
o-phenylphenol	90-43-7	Biocide used as a preservative, agricultural fungicide, disinfectant	1	0.33	0.03	0.03	0.03	3.09
Prosulfocarb	52888-80-9	Herbicide	1	0.33	0.03	0.03	0.03	4.65
4-Tert-octylphenol	140-66-9	Intermediate industrial compound	1	0.33	0.02	0.02	0.02	4.12
Benzo[b]fluoranthene	205-99-2	PAH, petroleum product	1	0.33	0.02	0.02	0.02	6.12
Isopropylbenzene	98-82-8	Crude oil (cumene)	1	0.33	0.02	0.02	0.02	3.66
1,3-Dichlorobenzene	541-73-1	Herbicides, insecticides, medicines, dyes	1	0.33	0.01	0.01	0.01	3.53
Benzo[a]pyrene	50-32-8	PAH, coal tar	1	0.33	0.01	0.01	0.01	6.04
Oxazepam	604-75-1	Pharmaceutical	1	0.33	0.01	0.01	0.01	3.34
Propazine	139-40-2	Herbicide	1	0.33	0.01	0.01	0.01	2.91

**The analysis of the compounds from piezometer R in November was absent due to loss of the sample by the courier. Rows in grey show plasticisers.

number of compounds detected during high water level period of Jan–May. The mean numbers of compounds detected per visit for D2 were 3(Aug–Dec) and 2 (Jan–May) and for Y the mean was 4 (Aug–Dec) and 3 (Jan–May) respectively.

This pattern was not seen within the surface waters or the HZ. Here the numbers of compounds detected were significantly and consistently lower than the Chalk with the median number of compounds detected being 2 in all three piezometers and the river throughout the study. The summary of the number of detects in different settings against the water levels are shown in Fig. 2. Fig. 2 A shows the temporal variation of the number of compounds detected in chalk D1, gravel D2 and Y as well as river sample SW and Fig. 2B summarises the temporal variation of the number of compounds detected within the HZ. Water levels at the individual sites are also shown.

4.2. Concentrations and identification of MOs

4.2.1. Overall maximum concentrations

Assessing MOs by concentration rather than by frequency of detection shows a very different pattern. For the site overall, there is less evidence of triazine herbicides or PAH, and instead plasticisers and industrial compounds dominate. The ten compounds with highest

concentrations, in decreasing order are: BPA 39 μg/L, DIBP 5 μg/L, caprolactam 3 μg/L, DEP and di-n-butyl phthalate both 1 μg/L, TCE 0.90 μg/L, 2-chlorophenyl isocyanate 0.85 μg/L, BHT and propyzamide 0.2 μg/L, drometrizole 0.15 μg/L (see Table 2). The median concentrations of the compounds detected more than once are presented in Fig. 3. This again highlights that greater numbers of compounds are found at higher concentration within the Chalk.

4.2.2. Characteristics of the different water compartments

4.2.2.1. Chalk groundwater. In Chalk groundwater the highest total MO concentration was in August 2013 (39.7 μg/L) with other high values in April (18.72 μg/L), November (10.52 μg/L) and May (7.64 μg/L). During the period of rising groundwater table and high groundwater levels in December–March before the subsequent recession in April the total MO was recorded as declining from 0.79 μg/L to 0.53 μg/L. The lowest total MO recorded in D1 was in June at 0.08 μg/L. This was also the lowest total MO recorded for any groundwater site.

The highest individual MO concentration was for BPA in August 2013 (39.66 μg/L); —over 30 times higher than the median of 1.21 μg/L. Other high concentrations were for DIBP was 5 μg/L in November, DEP in October and di-n-butyl phthalate in November both at 1 μg/L closely followed by TCE at 0.9 μg/L in October and 2-chloroprophyl isocyanate at 0.85 μg/L in July.

The main compounds were similar to the alluvium but there was a greater number of less-frequently detected compounds, some of which were PCPs, surfactants or food additives. Atrazine was detected on every visit but at relatively low concentrations 0.02 to 0.04 μg/L (med 0.04 μg/L). TCE was the second most common (92.3% with a range of 0.22–0.9 μg/L, med 0.445 μg/L). Other frequently detected compounds were atrazine desethyl 53.85%, simazine and BPA both at 38.46%, with less frequent detections of caffeine and 2-chlorophenyl isocyanate and the PCP 1(3H)-isobenzofuranone all at 23.08%, di-isobutyl phthalate and pharmaceuticals drometrizole and TTT all at 15.38%. Compounds detected only once included a range of PAH — fluoranthene, pyrene, chrysene and benz[a]anthracene, the plasticisers/flame retardants — diethyl phthalate, tributyl phosphate, tri-(2-chloroethyl) phosphate, di-n-butylphthalate and phthalic anhydride, surfactant — 4-tert-octylphenol, the food additives butylated hydroxyanisole (BHA), BHT, benzothiazole, and the biocide o-phenylphenol.

4.2.2.2. Alluvial groundwater. Total MOs were highest in piezometer Y in August 2013 at concentration of 3.4 μg/L, with two lesser peaks observed in February 1.42 μg/L and March 1.47 μg/L; this was nearly three times the median concentration of 0.5 μg/L. The lowest total MO concentration recorded in Y was 0.21 μg/L in June. Total MOs in piezometer D2 were highest in May at 1.06 μg/L nearly twice the median of 0.58 μg/L while the lowest was nearly half that at 0.26 μg/L in May. Overall range for the alluvium groundwater in Y has larger range and lower median concentration than D2; for Y range is 0.21–3.36 μg/L (median 0.5 μg/L) and for D2 it is 0.26–1.06 μg/L (median 0.58 μg/L).

TCE was detected on all visits (100%) in both Y and D2 piezometers. Concentrations for Y were in the range of 0.2–0.5 μg/L (med 0.3 μg/L) and D2 0.2–0.9 μg/L (med 0.4 μg/L). Other frequently detected compounds found in Y were atrazine detected in 84.6% with range of 0.01–0.02 μg/L (med 0.01 μg/L), BPA detected in 53.8% with a range of 0.02–0.6 μg/L (med 0.18 μg/L), atrazine desethyl detected 30.8% with a

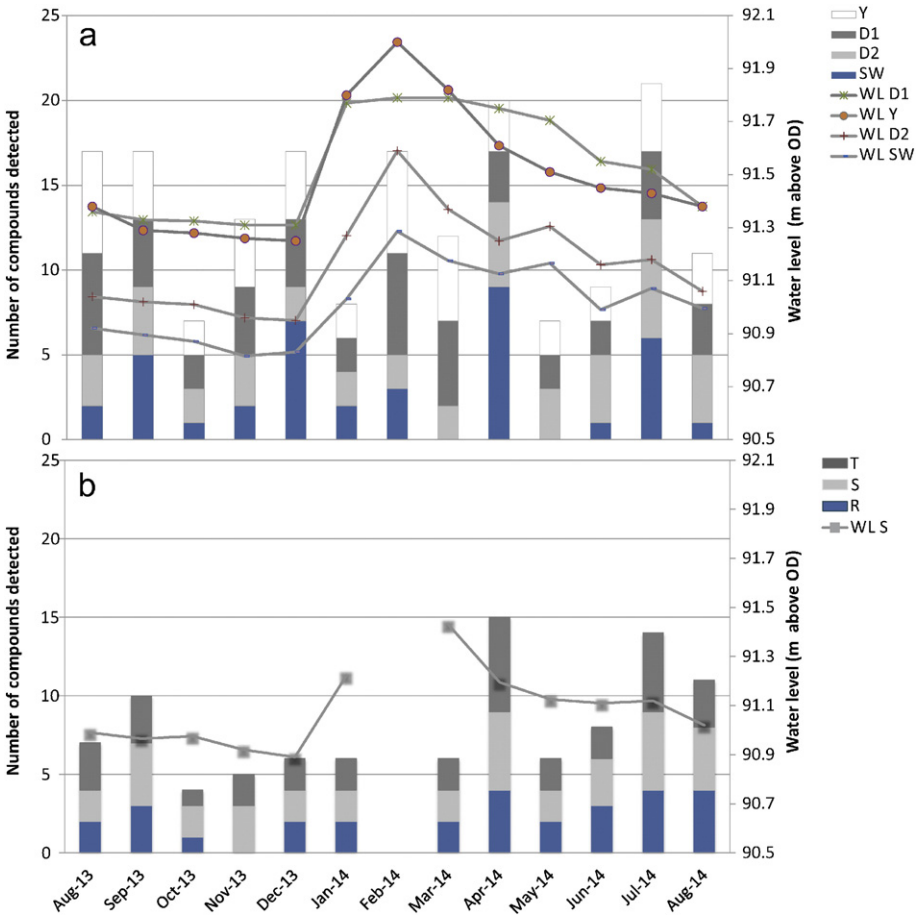

Fig. 2. Variation of detection frequency and water levels with time in a) groundwater and surface water and b) hyporheic zone. WL = water level data.

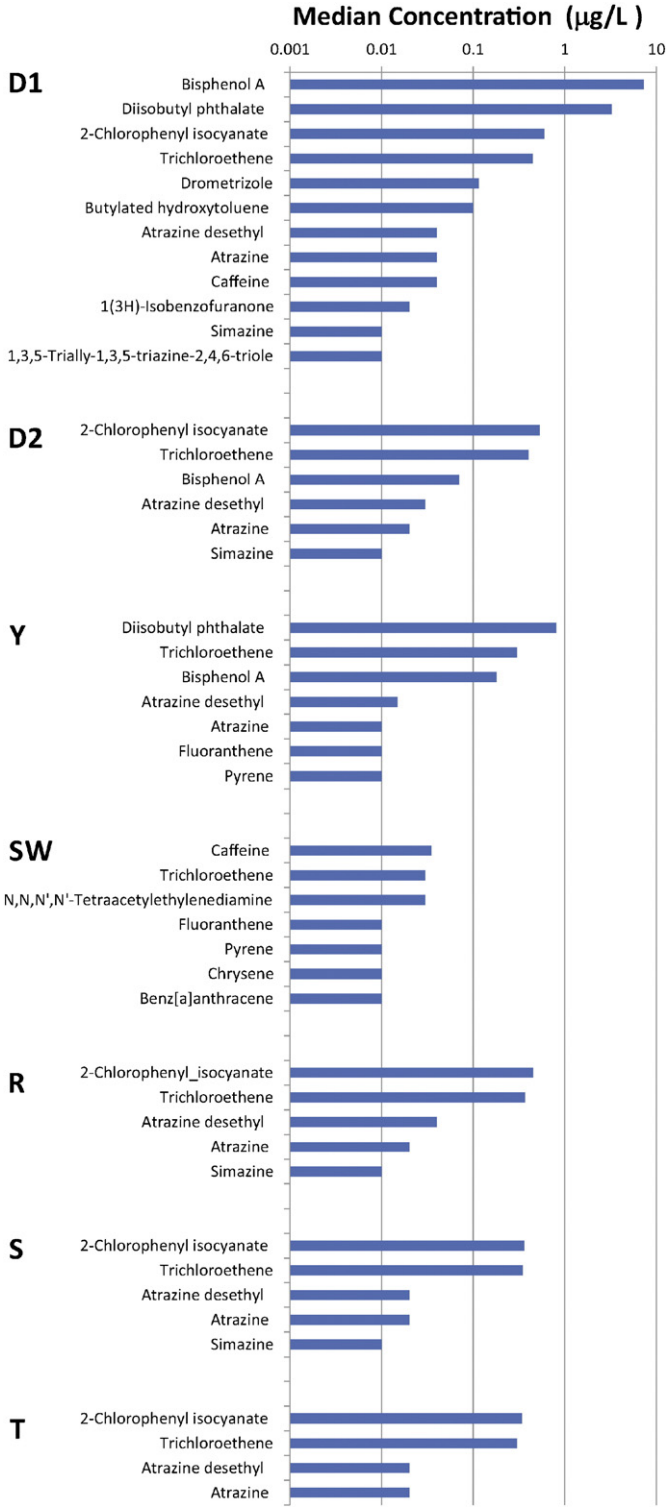

Fig. 3. Median concentrations of contaminant concentrations in different compartments that have been detected more than once (µg/L).

range of 0.01–0.02 µg/L (med 0.015 µg/L). The highest concentration for individual compounds within Y was for caprolactam (3.0 µg/L in August 2013) and 2-chlorophenyl isocyanate (0.28 µg/L in July). In D2 atrazine was detected in 92.3% with a range of 0.01–0.05 µg/L (med 0.02 µg/L) followed by simazine detected at 0.01 µg/L and 2-chlorophyl isocyanate with a range of 0.3–0.56 µg/L (med 0.53 µg/L) both detected in 30.8%. The highest individual compound concentration in D2 recorded was for TCE at 0.9 µg/L in October followed by 2-chloropropyl isocyanate at 0.56 µg/L in April and July. Other compounds detected in alluvial groundwater at site D2 were the industrial compounds isopropylbenzene, terpinyl acetate, 1,3-dichlorobenzene and the herbicide propazine. In piezometer Y caprolactam, the PAHs fluoranthene and pyrene, the plasticisers diisobutyl phthalate, triphenyl phosphate, and the pharmaceutical oxazepam were detected.

4.2.2.3. Surface water. In the River Lambourn the total MO range recorded was 0–0.42 µg/L, median 0.04 µg/L. The highest concentration recorded was in July. This was 10 times the median at 0.4 µg/L, the second highest, 0.34 µg/L recorded in December. During the months of March and May, no MOs were recorded at all.

The highest concentration detected within surface water was 0.28 µg/L of 2-chlorophenyl isocyanate which was detected only in July, followed by propyzamide at 0.2 µg/L in December.

The composition of the MOs was very different from that of groundwater. The two most frequently detected compounds were the PAHs fluoranthene with a range of 0.01–0.03 µg/L, median 0.01 µg/L and pyrene with a range of 0.01–0.02 µg/L, median 0.01 µg/L which were both detected in 54% of visits. Caffeine was the second mostly detected compound being detected 30.8% of visits with a range of 0.02–0.04 µg/L, median 0.035 µg/L. Other compounds that have been detected include TCE, the PAHs chrysene and benz(a)anthracene at 23.07%, and N,N,N′,N′-tetraacetylethylenediamine at 15.38%. Compounds that were detected only once included atrazine desethyl, atrazine, 2-chlorophenyl isocyanate, dimethyl phthalate, benzo[b]fluoranthene, benzo[a]pyrene cyclohexanone, terpinyl acetate seen in groundwater plus the pharmaceutical carbamazepine, and the pesticides propyzamide, prosulfocarb and diphenyl sulphide.

4.2.2.4. Hyporheic zone. The range of concentrations of MOs in the HZ were higher than those in surface water with medians considerably less than those in chalk and alluvium piezometers at the site Fig. 3. The total MOs ranged from 0.22 µg/L (in June in piezometer T) to 1.65 µg/L (in October in piezometer S).

The maximum concentration within the HZ was for BPA at 1 µg/L in R piezometer detected in October. This is followed by TCE at 0.7 µg/L was found in R in October and 2-chlorophenyl isocyanate at 0.5 µg/L in September in the same piezometer.

Within the HZ the number of different compounds detected was smaller than alluvium waters and significantly smaller than all other compartments (Fig. 4). The most frequently detected compounds were similar to those in groundwater. TCE was detected at all three sites on every visit between 0.1 and 0.7 µg/L. In piezometer R other compounds detected were atrazine (0.01–0.03 µg/L), atrazine desethyl (0.03–0.04 µg/L) and simazine (0.01 µg/L) followed by 2-chlorophenylisocyanate and terpinyl acetate. Piezometer S was very similar but with BPA and diphenyl sulphide also detected.

Atrazine was the second most detected compound within the HZ, with October being the only month where no compounds were detected in all 3 piezometers. Terpinyl acetate was only detected in April in all 3 hyporheic piezometers and was also found in surface water on the same visit.

5. Discussion

5.1. Comparison with other studies

Concentrations of MOs detected in this study are generally consistent with those reported by other groundwater studies, although we found overall fewer MOs with very few PCPs and pharmaceuticals. Lower concentrations were detected compared to Lapworth et al. (2015) for the Chalk aquifers of England and France for some MOs, particularly for caffeine, carbamazepine and atrazine, not unexpected given the lower number of samples. For MOs detected by both studies (atrazine, desethyl atrazine, caffeine and carbamazepine), Reh et al. (2013) found generally much higher frequencies of detection in a

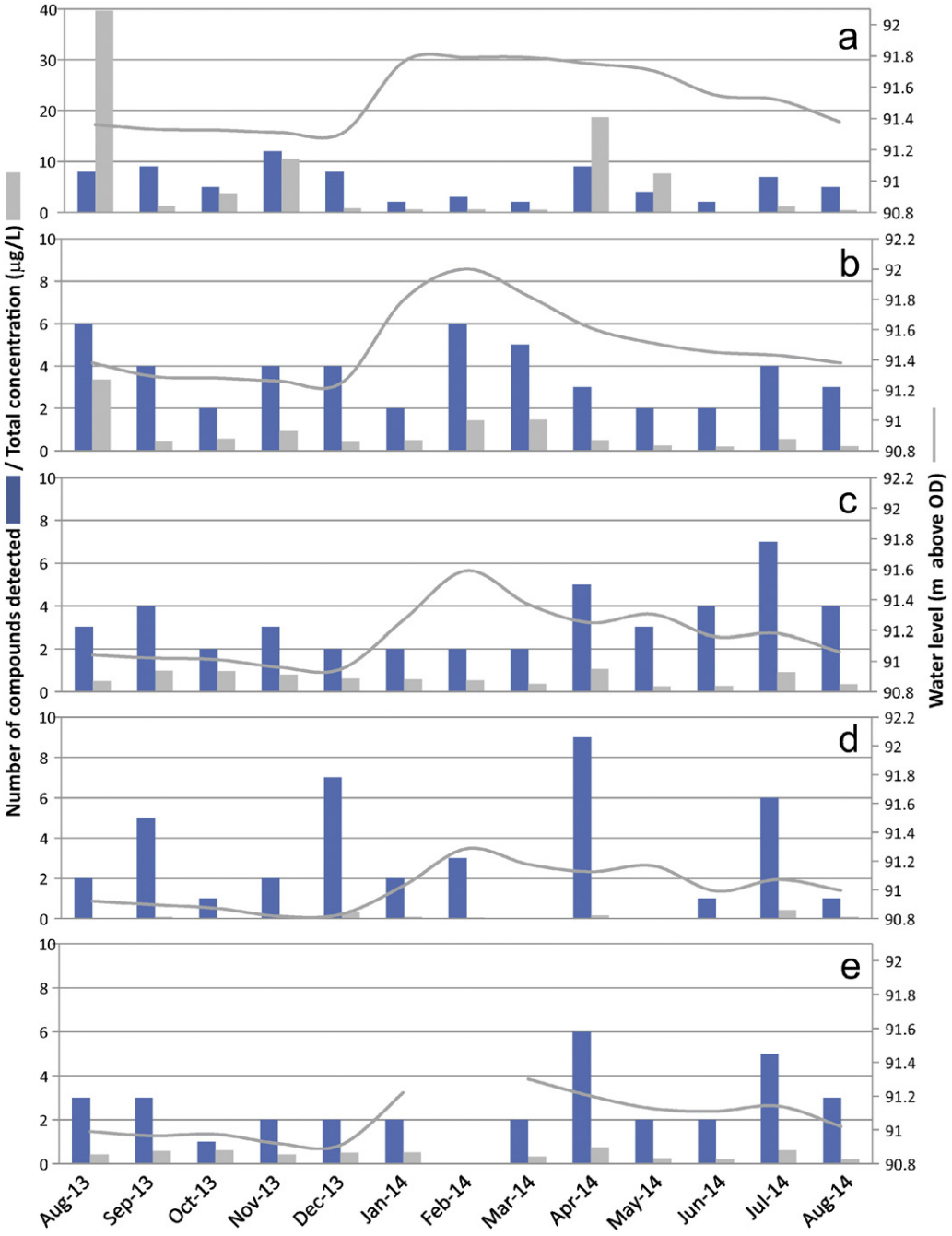

Fig. 4. Frequency of detection of MOs in water compartments: a) chalk groundwater D1, b) alluvial groundwater represented by gravel D2 and c) Y, d) River Lambourn, e) hyporheic zone represented by site T. Note that y-axis scale is different for Fig. 4a.

karst spring, due to their lower detection limit but relatively similar concentrations. The maximum concentration of caffeine within our study (0.1 µg/L) lies within the range for UK surface water (0.163–0.743 µg/L) reported by Petrie et al. (2014) but much lower than their maximum of 1.716 µg/L. However, carbamazepine concentration maximum concentration of 0.04 µg/L recorded in our study was significantly lower than that reported for surface water maximum within surface water of 0.684 µg/L.

The differences observed are likely to result from different inputs into the systems as well as analytical approaches. The absence of a greater variety of pharmaceuticals and personal care products in surface water suggests that upstream sources from sewage outfalls are diluted or assimilated due to in-stream processes and this is likely due to the relatively high baseflow inputs in this study area (CEH, 2015). Our finding show that aquifers can be the source of the MOs under conditions where the gradient is from the aquifer to surface water which is contrary to the usual perception that rivers disperse MOs to aquifers (Jurado et al., 2012; Pal et al., 2010). At Boxford we are likely seeing the impact of groundwater contaminated further up flow gradient on a seasonally gaining section of the river.

5.2. Hydrological controls

This study, using a programme of monthly monitoring, has shown that there is considerable variability in the concentration and number of MOs in all of the hydrological compartments other than HZ. In the

Chalk, water levels influence both the concentration of MOs and the overall number of compounds detected (Fig. 4). In surface water, rainfall is the main control on MO behaviour while there is no relationship for the HZ. The alluvial piezometers are influenced by both surface water and groundwater components and it is known that the dominant influence changes between low and high groundwater regimes (Allen et al., 2010). During the period of the study head reversal was observed on 3 occasions within the HZ piezometers.

This study demonstrated that the number and concentration of some MOs changes with time whereas others are detected at similar concentrations for all visits. Atrazine and TCE concentration changes in different compartments over the study period are shown in Fig. 5. Atrazine is present at low concentrations within all settings and does not seem to display a relationship linked to groundwater level. This suggests that it is present within the saturated zone. This behaviour is contrary to that reported for atrazine within karst springs of Germany (Hillebrand et al., 2014).

In contrast, TCE shows large changes in concentration with a peak value during the low water level period in October and a second peak corresponding to rising water levels in alluvial (Fig. 5a) and Chalk samples (Fig. 5b). Thereafter it declines with water level. This pattern is not present within surface water samples (Fig. 5c).

There are two possible mechanisms influencing MO response to water level changes with opposite consequences. During periods of recharge to the system, when groundwater levels will be high, the concentration of compounds present already within the system will decrease due to dilution. This was observed during January–March 2014. Conversely flushing out of the unsaturated zone of the catchment by rising groundwater levels could mobilise contaminants present in the unsaturated zone, either introducing new contaminants or increasing concentrations of existing ones. This may explain observations seen in April when a rise of both the number of compounds detected and their concentration was recorded. This is a commonly proposed mechanism controlling groundwater nitrate concentration fluctuations (Brouyère et al., 2004; Hong et al., 2007).

The spike in TCE in October is seen within both the alluvium and the Chalk simultaneously (Figs. 5a and 6b respectively), and the temporal trends in each compartment mirror each other. This traces the flow from the Chalk, with higher concentrations, to the alluvium in line with the head gradients for the majority of the study. This is also the case for atrazine although the concentrations are much lower. The high concentrations of TCE and atrazine seen in the River Lambourn in July and August 2014 (Fig. 5c) indicate a greater contribution of baseflow during this period. Understanding the behaviour of widespread contaminants such as atrazine and TCE can give us information on their source and pathway in this dynamic system.

The MOs detected and listed in Table 2 have a wide range of motilities in the aqueous environment, from mobile compounds such as

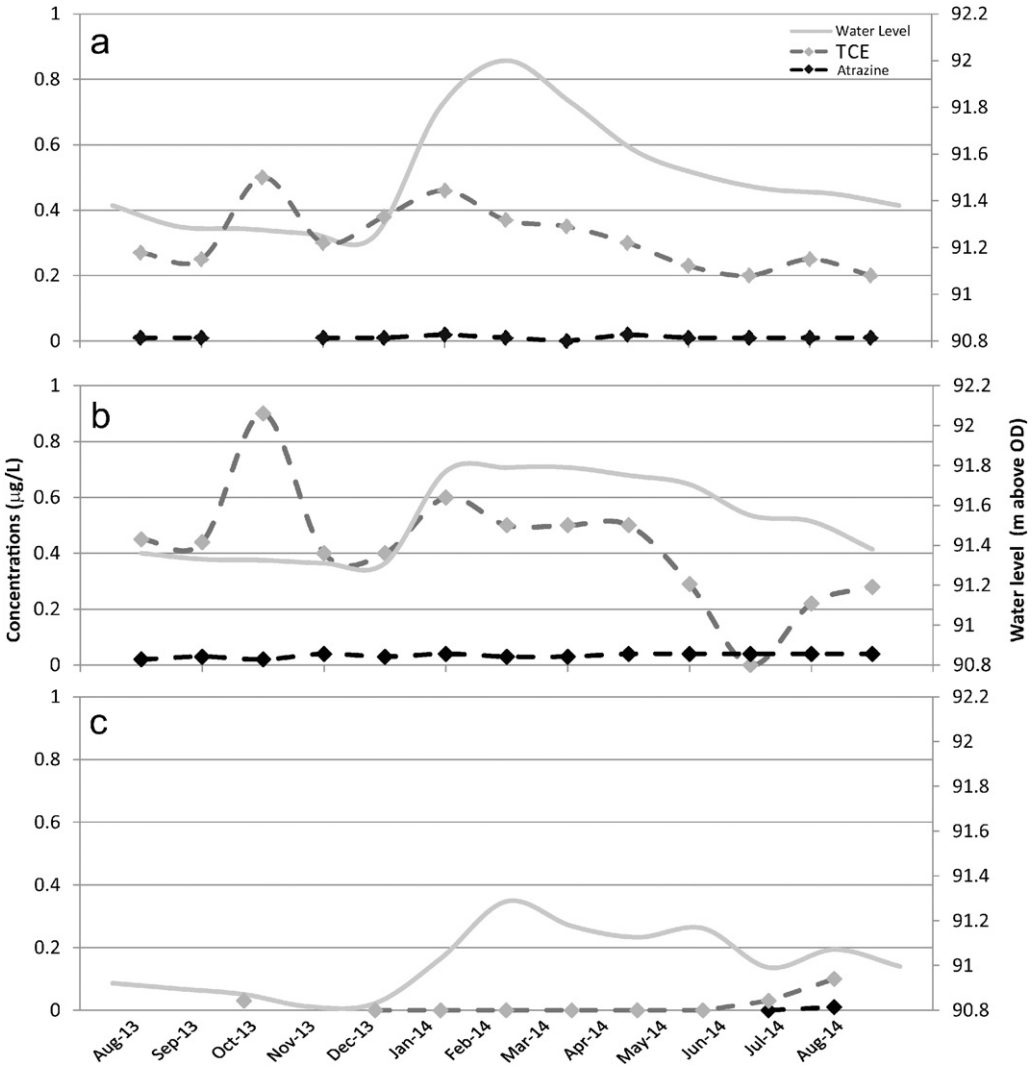

Fig. 5. Time series plots of atrazine, TCE concentrations and water levels in hydrological compartments: a) alluvium groundwater (Y); b) chalk groundwater (D1), and c) River Lambourn.

caffeine, caprolactam, TEAD and di-iso-butyl phthalate with log K_{ow} less than 1 to immobile PAHs and BHT with log K_{ow} greater than 5. Compounds with $K_{ow} < 1$ can be problematic for removal in drinking water treatment if they are also resistant to biological degradation (Petrović et al., 2003). There was no clear relationship between the K_{ow} values and the frequency of detection of compounds with those compounds found within the Chalk having marginally lower median K_{ow} value than compounds found within SW of 4.21 and 4.45 respectively. The detection of such immobile compounds could indicate a lack of suitable organic binding sites in the bulk of the chalk environment. However, peat layers are recorded in the alluvium at some locations in the study area and it is likely that these would be a sink for organic compounds.

The groundwater head is higher in the Chalk (see Fig. 2 and Fig. 4), therefore there is a hydraulic gradient from the Chalk to other compartments. This hydraulic connection is traced by the detection pattern of 2-chlorophenyl isocyanate which is likely to be a photo-degradation product of monuron, a banned phenylurea herbicide, (Pramauro et al., 1993). It is also a compound attractive to the cabbage root fly (Finch and Skinner, 1982). It was detected on 3 occasions within at least 4 compartments and twice on sampling round in just one compartment (Fig. 6). This compound was found on two occasions to have the greatest concentration within the Chalk and this together with the pattern of the concentrations detected on the same visit in different compartments confirms that the source of this compound is the Chalk rather than surface water. There is a notable absence of detections during high water table conditions. This combined with the intermittent occurrence in September, April and July suggest that in contrast to atrazine the source of this contaminant may be intermittent or controlled by rapid preferential pathways.

5.3. Conceptual models

The smallest numbers of compounds were detected in the HZ (n = 6–9). This is likely to be the result of attenuation due to higher microbial activity, and sorption processes in this zone compared to the other compartments. Within the river the number of compounds detected (n = 17) was almost double that found in the HZ. The environment with the greatest number of MOs detected was the Chalk with 26 compounds. These differences can be explained by changing pathways and sources of MOs operating at different time scales within the different compartments. Surface waters have shorter residence times and comprise a mixture of surface runoff and groundwater discharge. Solutes have a large potential to move in and out of the system quickly before they are degraded. Within groundwater, slower transport, particularly through the unsaturated zone and a consequently longer residence time (Wang et al., 2012), together with lower microbial activity in the Chalk (West and Chilton, 1997) allows MOs from both diffuse and point sources to persist. Under high water table conditions, where higher gradients are established between the Chalk and the river, there is more recharge to the Chalk groundwater, the concentration and number of compounds detected declines with an inverse relationship to the groundwater level rise. This strongly suggests that under these conditions there is rapid recharge of water in the unsaturated zone via activated fracture flow, with lower MO concentrations, causing a dilution of MOs at the water table.

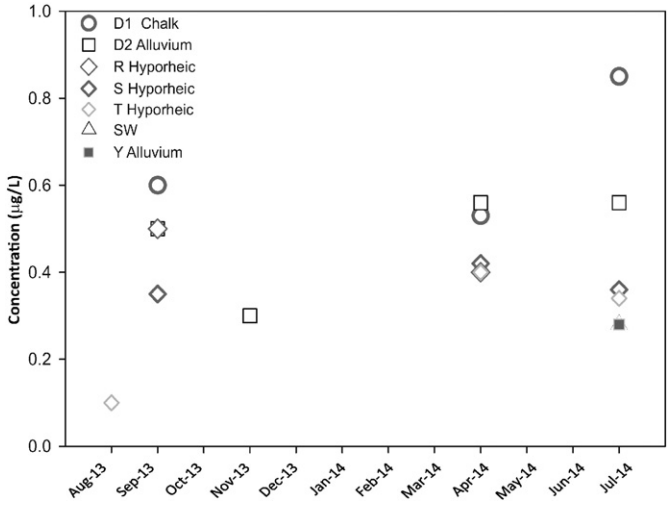

Fig. 6. Temporal variation in 2-chlorophenyl isocyanate in different compartments.

The piezometers in the alluvium have an intermediate number of MO detections (n = 10–11). The identity of these MOs suggests a mixed source. Piezometer Y shares 5 MOs with both D1 in the Chalk and D2 in the alluvium, an additional 3 with D1, and 3 not present in either. This could imply that Y has a different point source to that of D2 and D1 and this is consistent with water level evidence and the conceptual model of the site, which suggests additional up flow from the chalk into the gravels at this point as well as input from the barn which is up gradient. Overall Y has a MO signature that more closely resembles that of chalk D1 rather than the gravel piezometer D2. This further confirms the hypothesis that a chalk mound is present at Y and this influences the water chemistry (Allen et al., 2010).

The different response to water level changes contributes to the distribution of MOs in the various compartments and they can be distinct enough to be used to fingerprint sources of water entering the site. Carbamazepine was detected in the surface water, but not in groundwater, it is known to be highly persistent (Clara et al., 2004) in the environment and has been used by Wolf et al. (2012) to investigate the sewer leakages to groundwater. Equally, caffeine was detected in surface water Seiler et al. (1999) and has been suggested to indicate input of waste water and although in theory it is taken out during waste water processes there is evidence that this is often ineffective (Drewes et al., 2005; Sui et al., 2010).

5.4. Environmental risk

The cocktail of MOs detected contains a number that have already been classed as posing risks to drinking water or to the environment; these include plasticisers, pesticides, PAH and chlorinated solvents. Such compounds already have regulatory limits under the drinking water regulations for water used for public or private supply, environmental quality standards for surface water or are in the process of having groundwater threshold values established under the Water Framework Directive. The current European drinking water standards (Directive 98/83/EC) have a limit of 0.5 µg/L for total pesticides. However there are currently no limits in place for compounds that may be introduced into the environment together with pesticides, nor has the toxicity of such mixtures been widely studied. Some PAH (including anthracene), chlorinated solvents, pesticides (including atrazine and simazine), octyl and nonyl phenols and phthalates are regarded as priority substances under the Priority Substances Directive (2008/105/EC) and others including BPA, musk xylene and PFOS are subject to review.

A number of compounds are not removed by the standard water-treatment processes as reported by Stackelberg et al. (2004) and Sui et al. (2010), and the toxicity of their mixture needs to be evaluated further to understand the likely impacts on the health of ecologically sensitive compartments.

In this study, of the top 5 frequently detected compounds (excluding plasticisers) 4 are known to be used as pesticides, herbicides or their by-products. During the study the total pesticide concentrations did not exceed the 0.5 µg/L limit under the Drinking Water Directive. However two compounds, propyzamide at 0.2 µg/L and diphenyl sulphide at

0.13 μg/L exceeded the maximum concentration of 0.1 μg/L for individual pesticides.

Plasticisers are widely present and vary in their concentration. With potential increased use of plasticisers in existing and emerging industries there is potential for these compounds to accumulate in particular settings to concentrations which may have an impact on the ecosystem health and affect biological receptors negatively. The widespread presence of the plasticisers is of note regardless of their sources. This study has highlighted the need to have field blanks and lab blanks to effectively QC results and correct sample data for cross-contamination of plasticisers from tubing. There was no relationship between the K_{ow} values of these compounds and their persistence in the environment based on the results of this study.

As stated the Chalk aquifer is an extremely important source of drinking water. It also provides base flow to an extensive river system and directly or indirectly to wetlands and other sensitive ecosystems. Even in a rural setting, such as the study site, we see trace concentrations of anthropogenic MOs including industrial chemicals. As yet there are few data available to allow us to assess how important this may be or will become as pressure on water resources grows (Lapworth et al., 2015). If this resource is to be protected for future use there is a need to continue to monitor not only for regulated MOs which we know are present, such as pesticides and PAH, but also other compounds which are currently not covered by legislation. Additional long-term monitoring for these emerging MOs such as endocrine disruptors together with toxicology studies of these compounds, and mixtures of compounds, and their impact on already highly stressed ecosystems (RGS, 2012).

5.5. Wider implications

5.5.1. Impact on groundwater receptors

In the aqueous environment, periods of low rainfall, with consequent low river stages and low groundwater levels brings multiple stresses to the associated ecosystems. This study has shown that in some cases these low flows can lead to higher concentrations of contaminants in both surface water and groundwater due at least in part to lack of dilution of point sources. For many of the MOs detected we do not yet have sufficient, or indeed in many cases any, data to indicate at what concentration sectors of the ecosystem could be impacted, but it is clear that there must be increase in risk.

5.5.2. Impact on monitoring strategies

The seasonal variation in MOs, in terms of both concentrations and numbers of compounds, which has been demonstrated here, is likely to be typical of many settings where there is groundwater/surface water interaction and in other basins with high base flow contributions. Such variations have considerable implications for the design of monitoring strategies for these types of compound. Under the Water Framework Directive surveys for these compounds tend to be annual or quarterly at best and pressure on monitoring resources will mean that surveying continues throughout the year at a sustainable level, rather than focussing on periods where increased concentrations or numbers of MO are likely to be found. The risk of missing significant pulses of MOs in the aquatic environment is high and supports the wider use of passive sampling techniques (Coes et al., 2014; Vrana et al., 2014).

5.5.3. Use as tracers

A few studies have already employed emerging contaminants as environmental tracers in groundwater systems e.g. artificial sweeteners, nicotine, triclosan, DEET (Hillebrand et al., 2015; Sorensen et al., 2014). Emerging MOs provide a unique opportunity to investigate rapid and transient contaminant pathways and residence times, particularly relevant to karstic Chalk and fractured basement systems where conventional age tracers usually only provide information on the bulk characteristics of groundwater systems.

5.5.4. Research needs

Much more research is needed on this topic, and the focus of future research should include the use of MOs as natural tracers of groundwater flow in the subsurface and the use of passive sampling techniques to monitor changes in MOs. The identification of key compounds, and mixtures of compounds, which are likely to pose a risk in the future, such as persistent legacy MO compounds, as well as emerging organic is required. Modelling studies focussed on understanding the fate of emerging and legacy MOs within different hydrogeological settings needs to be carried out in order to understand MOs likely to pose a risk in the future under changing land-use, population and climate scenarios (e.g. Lu et al., 2015a, 2015b). Greater understanding is needed of the role of microbiological activity on the fate of MOs within the GSI such as HZ, zones of mixing of different water types for example wetland; potential attenuation in peat horizons. Further research is also needed on the toxicity of the compounds, their bioaccumulation within ecosystem compartments and their impact on ecosystem services relative to other stresses.

6. Conclusions

This study has captured the behaviour of MOs during the on-set of and subsequent recovery following the extreme high groundwater levels in the winter of 2013/2014 with high frequency monthly sampling. Key conclusions are:

- Trace MOs were detected in all hydrological compartments in a chalk lowland catchment including the hyporheic zone, groundwater and surface water;
- The greatest diversity of MOs was found in the Chalk compared to surface waters and the hyporheic zone using this GCMS broad screening method which screens for >1000 compounds and was attributed to greater residence time in groundwater;
- High frequency sampling has shown that the hydrologic regime influences the number and concentration of MOs detected in groundwater and surface water with the risk of missing high flow event pulses or high concentrations during low-flows. This has important implications for setting up long term monitoring for MOs including emerging organic compounds;
- By contrast, diffuse legacy MOs, such as atrazine, occur within the saturated zone almost ubiquitously and were found at consistently low concentrations in all compartments;
- The hyporheic zone had consistently lower numbers of compounds and concentrations. This new evidence shows that this compartment has an important role in natural attenuation of MOs, providing an important ecosystem service.

Acknowledgements

The authors are grateful to their colleagues Peter Williams, Lindsay Holowka and Joseph Thompson for their contribution to field sampling and to Wayne Civil of the Environment Agency National Laboratory Service for analysis and answering all our queries. The work described has been funded by the British Geological Survey (Natural Environment Research Council). This paper is published with the permission of the Executive Director, British Geological Survey (NERC).

References

Allen, D.J., Darling, W.G., Gooddy, D.C., Lapworth, D.J., Newell, A.J., Williams, A.T., Allen, D., Abesser, C., 2010. Interaction between groundwater, surface water and the hyporheic zone in a Chalk stream: a case study from the River Lambourn, UK. Hydrol. J. 5, 1125–1141.

Ascott, M., Lapworth, D.J., Gooddy, D.C., Sage, R.C., Karapanos, I., Ward, R., 12-17 April 2015. Impacts of Extreme flooding on Riverback filtration water quality. European Geosciences Union. EGU General Assembly 2015, Vienna, Austria (Unpublished) http://adsabs.harvard.edu/abs/2015EGUGA..17.1534A.

Bloomfield, J.P., Williams, R.J., Gooddy, D.C., Cape, J.N., Guha, P.M., 2006. Impacts of climate change on the fate and behaviour of pesticides in surface and groundwater — a UK perspective. Sci. Total Environ. 369, 163–177.
Brausch, J.M., Rand, G.M., 2011. A review of personal care products in the aquatic environment: environmental concentrations and toxicity. Chemosphere 82, 1518–1532.
Brouyère, S., Dassargues, A., Hallet, V., 2004. Migration of contaminants through the unsaturated zone overlying the Hesbaye chalky aquifer in Belgium: a field investigation. J. Contam. Hydrol. 72, 135–164.
Buerge, I.J., Poiger, T., Müller, M.D., Buser, H.-R., 2003. Caffeine, an anthropogenic marker for wastewater contamination of surface waters. Environ. Sci. Technol. 37, 691–700.
Burke, V., Duennbier, U., Massmann, G., 2011. Laboratory experiments on redox-sensitivity of organic trace pollutants in groundwater. Geophys. Res. Abstr. 13 (EGU2011-9821-1, EGU General Assembly 2011).
CEH, 2015. National River Flow Archive. http://www.ceh.ac.uk/data/nrfa/.
Chambers, J.E., Wilkinson, P.B., Uhlemann, S., Sorensen, J.P.R., Roberts, C., Newell, A.J., Ward, W.O.C., Binley, A., Williams, P.J., Gooddy, D.C., Old, G., Bai, L., 2014. Derivation of lowland riparian wetland deposit architecture using geophysical image analysis and interface detection. Water Resour. Res. 50, 5886–5905.
Clara, M., Strenn, B., Kreuzinger, N., 2004. Carbamazepine as a possible anthropogenic marker in the aquatic environment: investigations on the behaviour of carbamazepine in wastewater treatment and during groundwater infiltration. Water Res. 38, 947–954.
Coes, A.L., Paretti, N.V., Foreman, W.T., Iverson, J.L., Alvarez, D.A., 2014. Sampling trace organic compounds in water: a comparison of a continuous active sampler to continuous passive and discrete sampling methods. Sci. Total Environ. 473, 731–741.
Defra, 2015. Water Abstraction From Non-tidal Surface Water and Groundwater. https://www.gov.uk/government/statistics/water-abstraction-estimates.
Drewes, J.E., Hemming, J., Ladenburger, S.J., Schauer, J., Sonzogni, W., 2005. An assessment of endocrine disrupting activity changes during wastewater treatment through the use of bioassays and chemical measurements. Water. Environ. Res. 12–23.
Engelhardt, I., Piepenbrink, M., Trauth, N., Stadler, S., Kludt, C., Schulz, M., Schüth, C., Ternes, T.A., 2011. Comparison of tracer methods to quantify hydrodynamic exchange within the hyporheic zone. J. Hydrol. 400, 255–266.
Finch, S., Skinner, G., 1982. Trapping cabbage root flies in traps baited with plant extracts and with natural and synthetic isothiocyanates. Entomol Exp Appl 31.
Focazio, M.J., Kolpin, D.W., Barnes, K.K., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Barber, L.B., Thurman, M.E., 2008. A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States: II) untreated drinking water sources. Sci. Total Environ. 402, 201–216.
Freitas, J.G., Rivett, M.O., Roche, R.S., Durrant, M., Walker, C., Tellam, J.H., 2015. Heterogeneous hyporheic zone dechlorination of a TCE groundwater plume discharging to an urban river reach. Sci. Total Environ. 505, 236–252.
Griebler, C., Avramov, M., 2015 Mar 1. Groundwater ecosystem services: a review. Freshwat. Sci. 34 (1), 355–367.
Halling-Sørensen, B., Nors Nielsen, S., Lanzky, P.F., Ingerslev, F., Holten Lützhøft, H.C., Jørgensen, S.E., 1998. Occurrence, fate and effects of pharmaceutical substances in the environment — a review. Chemosphere 36, 357–393.
Hillebrand, O., Nödler, K., Geyer, T., Licha, T., 2014. Investigating the dynamics of two herbicides at a karst spring in Germany: consequences for sustainable raw water management. Sci. Total Environ. 482, 193–200.
Hillebrand, O., Nödler, K., Sauter, M., Licha, T., 2015. Multitracer experiment to evaluate the attenuation of selected organic micropollutants in a karst aquifer. Sci. Total Environ. 506, 338–343.
Hong, N., White, J.G., Weisz, R., Gumpertz, M.L., Duffera, M.G., Cassel, D.K., 2007. Groundwater nitrate spatial and temporal patterns and correlations. Vadose Zone J. 6, 53–66.
Jurado, A., Vàzquez-Suñé, E., Carrera, J., López de Alda, M., Pujades, E., Barceló, D., 2012. Emerging organic contaminants in groundwater in Spain: a review of sources, recent occurrence and fate in a European context. Sci. Total Environ. 440, 82–94.
Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., Buxton, H.T., 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: a national reconnaissance. Environ. Sci. Technol. 36, 1202–1211.
Kümmerer, K., 2009. The presence of pharmaceuticals in the environment due to human use — present knowledge and future challenges. J. Environ. Manag. 90, 2354–2366.
Lapworth, D.J., Baran, N., Stuart, M.E., Manamsa, K., Talbot, J., 2015. Persistent and emerging micro-organic contaminants in Chalk groundwater of England and France. Environ. Pollut. (Online view).
Lapworth, D.J., Baran, N., Stuart, M.E., Ward, R.S., 2012. Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. Environ. Pollut. 163, 287–303.
Lewandowski, J., Putschew, A., Schwesig, D., Neumann, C., Radke, M., 2011. Fate of organic micropollutants in the hyporheic zone of a eutrophic lowland stream: results of a preliminary field study. Sci. Total Environ. 409, 1824–1835.
Loos, R., Locoro, G., Comero, S., Contini, S., Schwesig, D., Werres, F., Balsaa, P., Gans, O., Weiss, S., Blaha, L., Bolchi, M., Gawlik, B.M., 2010. Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. Water Res. 44, 4115–4126.
Lu, Q., Zhu, R.L., Yang, J., Li, H., Liu, Y.D., Lu, S.G., Luo, Q.S., Lin, K.F., 2015b. Natural attenuation model and biodegradation for 1, 1, 1-trichloroethane contaminant in shallow groundwater. Front. Microbiol. 6, 839. http://dx.doi.org/10.3389/fmicb.2015.00839.
Lu, Q., Johnson, A.C., Jürgens, M.D., Sweetman, A., Jin, L., Whitehead, P., 2015a. The distribution of polychlorinated biphenyls (PCBs) in the River Thames catchment under the scenarios of climate change. Sci. Total Environ. 533, 187–195.
Luo, Y., Guo, W., Ngo, H.H., Nghiem, L.D., Hai, F.I., Zhang, J., Liang, S., Wang, X.C., 2014. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Sci. Total Environ. 473–474, 619–641.
Newell, A.J., Sorensen, J.P., Chambers, J.E., Wilkinson, P.B., Uhlemann, S., Roberts, C., Gooddy, D.C., Vane, C.H., Binley, A., 2015. Fluvial response to late Pleistocene and Holocene environmental change in a Thames chalkland headwater: the Lambourn of southern England. Proc. Geol. Assoc. 126 (6), 683–697.
Pal, A., Gin, K.Y.-H., Lin, A.Y.-C., Reinhard, M., 2010. Impacts of emerging organic contaminants on freshwater resources: review of recent occurrences, sources, fate and effects. Sci. Total Environ. 408, 6062–6069.
Petrie, B., Barden, R., Kasprzyk-Hordern, B., 2014. A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. Water Res. 72, 3–27.
Petrović, M., Gonzalez, S., Barceló, D., 2003. Analysis and removal of emerging contaminants in wastewater and drinking water. TrAC 22, 685–696.
Pramauro, E., Vincenti, M., Augugliaro, V., Palmisano, L., 1993. Photocatalytic degradation of monuron in aqueous titanium dioxide dispersions. Environ. Sci. Technol. 27, 1790–1795.
Reh, R., Licha, T., Geyer, T., Nödler, K., Sauter, M., 2013. Occurrence and spatial distribution of organic micro-pollutants in a complex hydrogeological karst system during low flow and high flow periods, results of a two-year study. Sci. Total Environ. 443, 438–445.
RGS, 2012. Water Policy in the UK: The Challenges Royal Geographical Society with IBG RGS-IBG Policy Briefing.
Schwarzbauer, J., Heim, S., Brinker, S., Littke, R., 2002. Occurrence and alteration of organic contaminants in seepage and leakage water from a waste deposit landfill. Water Res. 36, 2275–2287.
Seiler, R.L., Zaugg, S.D., Thomas, J.M., Howcroft, D.L., 1999. Caffeine and pharmaceuticals as indicators of waste water contamination in wells. Ground Water 37, 405–410.
Sorensen, J.P.R., Lapworth, D.J., Nkhuwa, D.C.W., Stuart, M.E., Gooddy, D.C., Bell, R.A., Chirwa, M., Kabika, J., Liemisa, M., Chibesa, M., 2014. Emerging contaminants in urban groundwater sources in Africa. Water Res. 72, 51–63.
Stackelberg, P.E., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Henderson, A.K., Reissman, D.B., 2004. Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant. Sci. Total Environ. 329, 99–113.
Stuart, M.E., Lapworth, D.J., Crane, E.J., Hart, A., 2012. Review of risk from potential emerging contaminants in UK groundwater. Sci. Total Environ. 416, 1–21.
Stuart, M.E., Lapworth, D.J., Thomas, J., Edwards, L., 2014. Fingerprinting groundwater pollution in catchments with contrasting contaminant sources using microorganic compounds. Sci. Total Environ. 468, 564–577.
Sui, Q., Huang, J., Deng, S., Yu, G., Fan, Q., 2010. Occurrence and removal of pharmaceuticals, caffeine and DEET in wastewater treatment plants of Beijing, China. Water Res. 44, 417–426.
Vrana, B., Klučárová, V., Benická, E., Abou-Mrad, N., Amdany, R., Horáková, S., Draxler, A., Humer, F., Gans, O., 2014. Passive sampling: an effective method for monitoring seasonal and spatial variability of dissolved hydrophobic organic contaminants and metals in the Danube River. Environ. Pollut. 184, 101–112.
Ward, A.S., Cwiertny, D.M., Kolodziej, E.P., Brehm, C.C., 2015 May 8. Coupled reversion and stream-hyporheic exchange processes increase environmental persistence of trenbolone metabolites. Nat. Commun. 6. http://dx.doi.org/10.1038/ncomms8067.
Wang, L., Stuart, M.E., Bloomfield, J.P., Butcher, A.S., Gooddy, D.C., McKenzie, A.A., Lewis, M.A., Williams, A.T., 2012. Prediction of the arrival of peak nitrate concentrations at the water table at the regional scale in Great Britain. Hydrol. Proced. 26, 226–239.
West, J.M., Chilton, P.J., 1997. Aquifers as environments for microbiological activity. Q. J. Eng. Geol. Hydrogeol. 30, 147–154.
Wheater, H.S., Peach, D., 2004. Developing interdisciplinary science for integrated catchment management: the UK lowland catchment research (LOCAR) programme. Int. J. Water Resour. Devel. 20, 369–385.
Wode, F., van Baar, P., Dünnbier, U., Hecht, F., Taute, T., Jekel, M., Reemtsma, T., 2015. Search for over 2000 current and legacy micropollutants on a wastewater infiltration site with a UPLC-high resolution MS target screening method. Water Res. 69, 274–283.
Wolf, L., Zwiener, C., Zemann, M., 2012. Tracking artificial sweeteners and pharmaceuticals introduced into urban groundwater by leaking sewer networks. Sci. Total Environ. 430, 8–19.